

CuO CATHODE IN LITHIUM CELLS I. INFLUENCE OF THE DECOMPOSITION CONDITIONS OF $\text{Cu}(\text{OH})_2$ ON THE PROPERTIES OF CuO

P. NOVÁK, B. KLÁPŠTĚ and P. PODHÁJECKÝ

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Prague 10 (Czechoslovakia)

(Received January 24, 1985)

Summary

The electrochemical properties of CuO in galvanic cells with a lithium anode show a correlation with the conditions of its preparation from $\text{Cu}(\text{OH})_2$. To attain the highest cell discharge capacity and a favourable discharge voltage, the $\text{Cu}(\text{OH})_2$ must be decomposed at 300 °C for 2 h. Differences in the properties of CuO prepared under different conditions are attributed to a variable content of chemically bound water in the form of residual OH groups. No other phases were detected in the CuO structure by X-ray analysis.

Introduction

The Li-CuO system, with a discharge voltage of 1.0 - 1.4 V, is one of the few lithium cells suitable to replace the classical Leclanché cells [1 - 3]. Both the highest attainable cell capacity and the discharge voltage are influenced by the method of preparation of the electroactive CuO material.

It has been shown in our preceding work [4] that thermal decomposition of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ leads to CuO samples with an electrochemical capacity which exceeds 90% C_t (theoretical specific capacity $C_t = 0.674$ A h/g of CuO). The discharge voltage of cells prepared from them, however, was initially too high (1.7 V) and could cause problems in practical applications. This was attributed [4] to the presence of contaminants, such as $\text{Cu}_4(\text{OH})_6\text{SO}_4$, which could not be removed during the preparation of the active material. The purpose of the work presented here was to prepare very pure copper hydroxide and then to decompose it under conditions which resulted in optimum cell parameters.

Experimental

Preparation of CuO

Very pure copper oxide can be obtained by decomposition of $\text{Cu}(\text{OH})_2$ prepared by precipitation of a $\text{Cu}(\text{NO}_3)_2$ solution with ammonia. Impurities such as $\text{Cu}_2(\text{OH})_3\text{NO}_3$ can be either washed out with water or decomposed at temperature under 300°C [5] to give CuO and gaseous products.

To find the optimum conditions for the precipitation, we studied the influence of the solution temperature. The best product was obtained as follows. An aqueous solution of approximately 1M reagent grade $\text{Cu}(\text{NO}_3)_2$ was precipitated by boiling with 10% reagent grade NH_4OH (both Lachema, ČSSR) in the presence of several per cent of NH_4NO_3 . The precipitated hydroxide was partially dehydrated during boiling for 8 h, washed and decanted several times, filtered, and dried at 105°C in air. The resulting non-stoichiometric mixture of CuO and $\text{Cu}(\text{OH})_2$ was used to study the influence of the temperature and the duration of the thermal decomposition on the electrochemical properties of CuO .

The decomposition took place in an evacuated glass ampoule placed in an electric oven. Comparative experiments were done with the glass ampoule open to the atmosphere. For temperatures of 500°C and higher, an open porcelain mortar was used.

Electrochemical measurements

Thin electrodes [6, 7] were discharged galvanostatically at room temperature with a current corresponding to a 10 h discharge. The cathode mix consisted of equal parts of CuO and Teflonised carbon black [8], *i.e.*, 75 wt.% acetylene black P1042 (Stickstoffwerke, Piesteritz, GDR) for better conductivity, and 25 wt.% Teflon GP-1 (ICI, U.K.). This was rolled onto a nickel gauze, a part of which served as current lead (square density 0.285 kg/m^2 , wire diameter 0.05 mm, mesh size 0.08 mm). The CuO content was about 15 mg/cm^2 . The cathodes were discharged in a glass cell with two large lithium counter-electrodes and a Li reference electrode in an excess of 1M LiClO_4 in propylene carbonate (containing less than 50 ppm of water) electrolyte (both Fluka). The cathode capacity (in % C_t) was measured to a discharge potential of 1.0 V against the Li reference electrode.

To detect electroactive impurities, voltammetric curves in the range 2.8 - 0.8 V *vs.* Li/Li^+ at a sweep rate of 3 mV/min were measured under the same conditions.

For comparison, the discharge curves of "thick" electrodes were also measured. These were prepared by pressing about 120 mg of the cathode mix at 200 MPa onto a copper mesh as a central current collector. Circular tablets of 10 mm dia. were discharged in a glass ampoule with an excess of electrolyte and lithium at a current corresponding to a 100 h discharge. The composition of the cathode and the electrolyte was the same as with the thin model electrodes.

The cells were assembled in a dry box under an argon atmosphere containing less than 20 ppm H₂O.

Non-electrochemical measurements

The copper content of the active material was determined by complexometric titration [9] and the Cu(II), Cu(I), and Cu metal contents were determined by a polarographic method [10]. The BET specific surface area, granulometric composition, thermogravimetric analysis, X-ray and XPS diagrams of CuO samples were measured by standard methods.

The quantities of water and oxygen evolved at elevated temperatures were determined as follows [11]. A weighed amount (0.5 g) of CuO was placed in a thermostatically controlled U-tube through which argon was passed at a constant rate. The tube was slowly heated (1 °C/min) up to 500 °C. The water and oxygen contents of the outlet gas were measured separately.

Results and discussion

Thermogravimetry of the partially decomposed Cu(OH)₂ revealed that the lowest temperature necessary for complete decomposition is 300 °C. Since our previous work [4] showed that prolonged heating of CuO causes degradation of its electrochemical properties, we investigated the effect of the time of decomposition of the hydrated CuO at 300 °C on the discharge capacity of the product. The results (in %C_t) are shown in Fig. 1. It can be seen that a 2 h decomposition leads to a product giving the highest capacity, nearly 100% C_t, regardless of whether it was prepared under vacuum or in air. The capacity is lower after a shorter decomposition time, since undecomposed Cu(OH)₂ remains in the material. This can be seen from Fig. 2, where the solid line is the voltammetric curve of the best CuO sample and the dashed line corresponds to incompletely decomposed Cu(OH)₂. The indistinct peaks close to 2 V probably correspond to the reduction of oxygen and water adsorbed on CuO [12], since no significant impurities were found in the CuO samples. The peak at 1.8 V, corresponding to reduction of Cu(OH)₂, diminishes with prolonged heating, while the peak at 1.1 V, corresponding to the reduction of CuO, increases. At potentials below 1 V intercalation of Li⁺ ions into the carbon black present in the cathode mix takes place [13].

When the heating time exceeded 2 h the capacity decreased to 80 - 88% C_t (Fig. 1) and did not change further. Increasing the decomposition temperature had a similar effect (Table 1); less active forms of CuO with a capacity of 77 - 88% C_t were produced. A similar result was obtained after 4 h decomposition at 900 °C in air. The decrease in capacity is probably related to changes in the kinetics of solid-phase reactions [14 - 16] due to the changing concentration of defects in the CuO lattice during heating, since no differences in the chemical composition of the samples were found by chemical

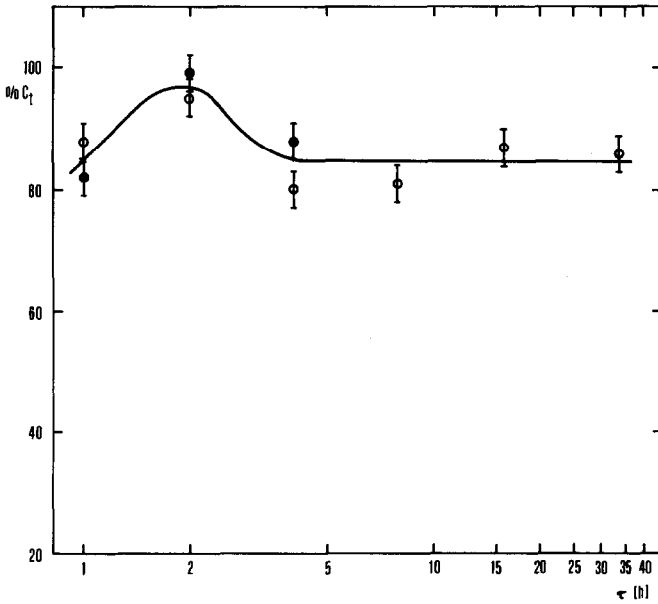


Fig. 1. Dependence of discharge capacity (% C_t) on the decomposition time (h) of the sample. Thin electrodes, 10 h discharge rate; ○, decomposition at 300 °C under vacuum; ●, 300 °C in air.

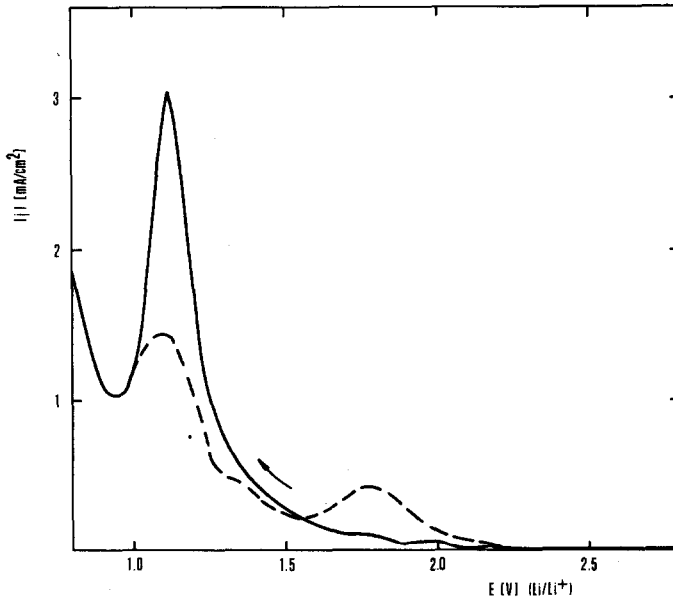


Fig. 2. Voltammogram curves. —: most active CuO, decomposed for 2 h at 300 °C in air (99% C_t); - - -: sample containing $\text{Cu}(\text{OH})_2$ (72% C_t).

TABLE 1

Dependence of discharge capacity ($\%C_t$) on the time and temperature of decomposition in the presence of air
Thin electrodes at a 10 h discharge rate

Decomposition temperature (°C)	Decomposition time	
	1 h	2 h
300	82	99
350	81	81
400	88	88
500	79	84
600	77	86

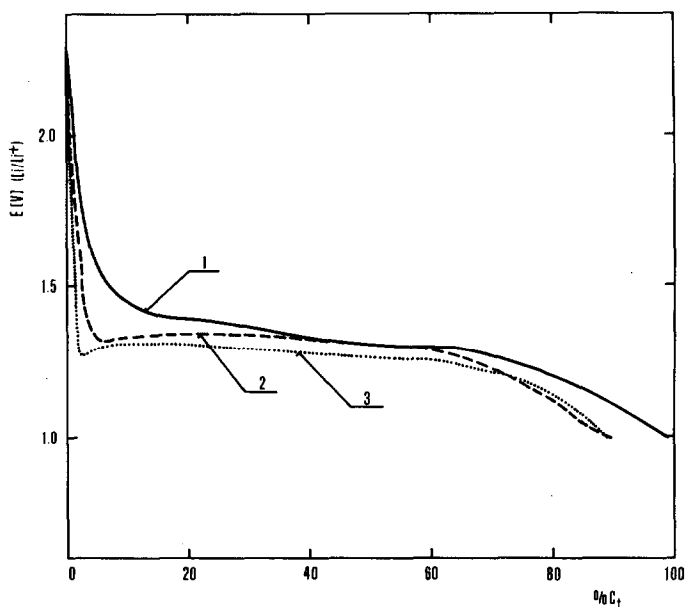


Fig. 3. Discharge curves for thin CuO electrodes at 10 h discharge rate. 1, Sample decomposed for 2 h at 300 °C in air; 2, as 1 but 400 °C; 3, as 1 but 4 h at 900 °C.

analysis. Their purity was substantiated by XPS diagrams, which showed only traces of sodium and carbon. The specific surface area, about 2 m²/g, and the granulometric composition of the samples were practically constant.

The discharge curves of samples obtained by decomposition at various temperatures are shown in Fig. 3; the discharge potential decreases with increasing decomposition temperature. Curve 1 (99% C_t , 2 h at 300 °C) shows two reduction steps with a similar discharge potential (1.4 and 1.3 V), suggesting the presence of two substances with different reduction kinetics. X-ray analysis, however, showed the presence of only one phase, *i.e.*, monoclinic CuO, in all samples under study. The differences in the electrochemical

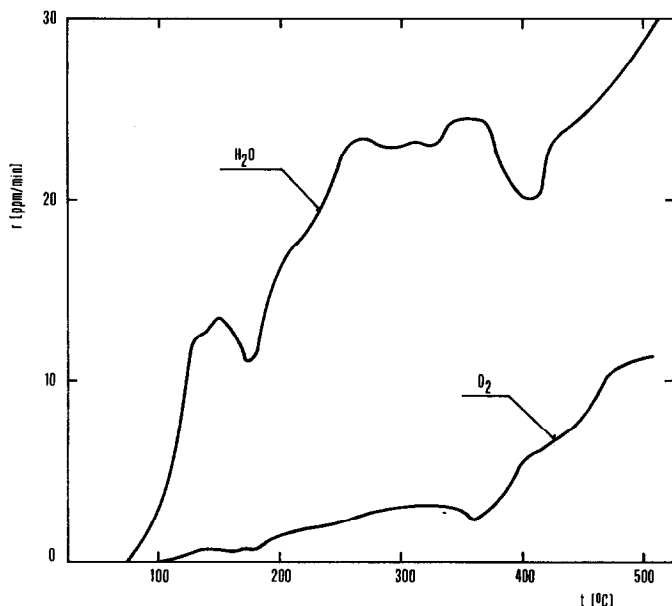


Fig. 4. Rate of desorption, r (ppm/min), of water and oxygen from the most active CuO sample during increasing temperature at $1\text{ }^{\circ}\text{C}/\text{min}$.

activity can rather be attributed to changes in the concentration of defects in the crystal lattice and in the residual content of chemically bound water. This explanation is supported by the presence of the indistinct peak at 1.8 V on the voltammetric curve of the best CuO sample (Fig. 2), corresponding to reduction of $\text{Cu}(\text{OH})_2$, as mentioned above. Hence, it seems that some residual OH groups are present in the active form of CuO. It is remarkable in this respect that OH groups are responsible for the high discharge capacity of active forms of MnO_2 in aqueous medium [17 - 19].

To substantiate this point of view further, we measured the rate of desorption of water and oxygen from the CuO samples during heating; the results for the most active sample are shown in Fig. 4. The physically adsorbed water was desorbed below $200\text{ }^{\circ}\text{C}$ while the rate of desorption was highest in the range from 260 to $370\text{ }^{\circ}\text{C}$. This is due to the gradual decomposition of $\text{Cu}(\text{OH})_2$ residues in the CuO structure; with less active samples the residues of bound water were eliminated by the higher decomposition temperature and/or prolonged heating. In the temperature interval considered, only a very small quantity of oxygen was released from the sample (Fig. 4), *i.e.*, 0.1% up to $400\text{ }^{\circ}\text{C}$, hence, there was no decomposition of CuO. (The total quantity of water desorbed up to $500\text{ }^{\circ}\text{C}$ was less than $0.8\text{ wt.}\%$, *i.e.*, also small.)

The discharge measurements on thin model electrodes, which yielded data about a large number of cathode material samples, were in agreement with results obtained on the thicker electrodes which contained more active material and were subject to a slower discharge (Fig. 5).

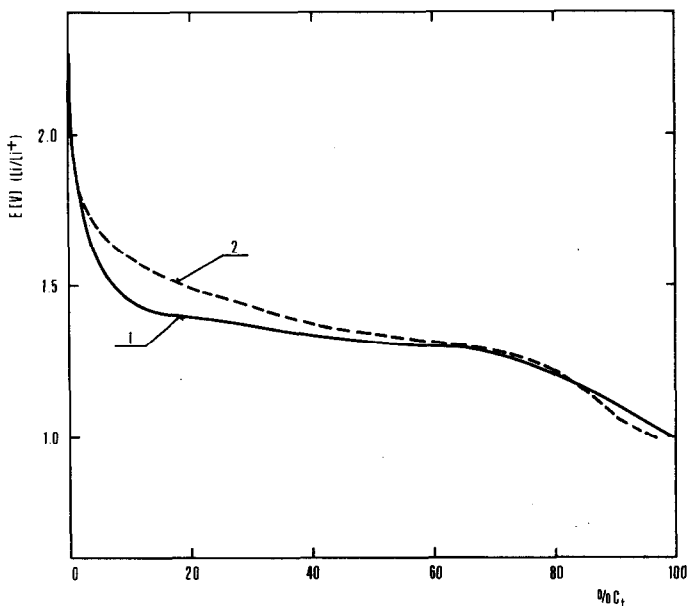


Fig. 5. Discharge curves for electrodes from samples decomposed for 2 h at 300 °C in air. 1, Thin electrode, 10 h discharge rate. 2, Thick (practical) electrode, 100 h discharge rate.

Conclusions

Copper oxide cathodes for lithium batteries can best be prepared from CuO formed by thermal decomposition of pure, hydrated copper oxide under defined conditions (300 °C, 2 h in our case). Shorter decomposition times reduce the capacity of the sample due to the presence of Cu(OH)₂. Longer decomposition times or higher temperatures cause removal of the residual OH groups present in the active CuO structure, resulting in a decrease of both the discharge potential and the capacity. It is still possible, however, that the differences in the electrochemical behaviour may be attributed to a different defect concentration in the crystallographic lattice rather than to the presence of different phases in varying proportions.

Acknowledgements

The authors are indebted to Dr V. Manev (Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia) for desorption rate measurements, to Dr V. Valvoda (Charles University, Prague) for X-ray analyses, and Drs L. Kavan, P. Papež and Z. Záborský (this Institute) for XPS, chemical, and granulometric analyses.

References

- 1 M. Hughes, N. A. Hampson and S. A. G. R. Karunathilaka, *J. Power Sources*, **12** (1984) 83.
- 2 R. Bates and Y. Jumel, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, p. 76.
- 3 T. Iijima, Y. Toyoguchi, J. Nishimura and H. Ogawa, *J. Power Sources*, **5** (1980) 99.
- 4 P. Podhájecký, B. Klápště, P. Novák, J. Mrha, R. Moshtev, V. Manev and A. Nassalevska, *J. Power Sources*, **14** (1985) 269.
- 5 M. N. Nabiev, T. Kh. Taksanova and V. K. Khakimova, *Uzb. Khim. Zh.*, **17** (1973) 13.
- 6 V. Manev, R. Moshtev, A. Nassalevska, A. Gushev and G. Pistoia, *Solid State Ionics*, **13** (1984) 181.
- 7 R. Moshtev, V. Manev, A. Nassalevska and G. Pistoia, *Solid State Ionics*, **14** (1984) in press.
- 8 I. Iliev, J. Mrha, S. Gamburtsev and A. Kaisheva, *J. Appl. Electrochem.*, **5** (1975) 291.
- 9 R. Přibil, *Komplexometrie*, SNTL, Praha, 1977, p. 191.
- 10 V. Papež and J. Večerník, *Anal. Lett.*, **17** (A19) (1984) 2183.
- 11 V. Manev, *Thesis*, Central Laboratory of Electrochemical Power Sources, Sofia, 1985.
- 12 J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. III, Longmans, London, 1923, p. 132.
- 13 K. M. Abraham and S. B. Brummer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, p. 387.
- 14 R. Bates and Y. Jumel, in G. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, p. 91.
- 15 V. V. Boldyrev, *Kinet. Katal.*, **1** (1960) 203.
- 16 M. V. Pticyn and K. I. Tichonov, *Elektrokhimiya*, **20** (1984) 160.
- 17 J. Brenet, in D. H. Collins (ed.), *Batteries*, Pergamon Press, New York, 1963, p. 357.
- 18 J. Brenet, in D. H. Collins (ed.), *Power Sources*, Pergamon Press, Oxford, 1967, p. 39.
- 19 K. Le Tran and J. Brenet, *C. R. Acad. Sci., Ser. C*, **264** (1967) 1517.